Impact of New Laboratory Studies of N2O5 Hydrolysis on Global Model Budgets of Tropospheric Nitrogen Oxides, Ozone, and OH

Impact of new laboratory studies of N_2O_5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH

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[1] We investigate the impact of new laboratory studies of N_2O_5 hydrolysis in aerosols on global model simulations of tropospheric chemistry. We use data from these new studies to parameterize the reaction probability (γ_{N2O5}) in the GEOS-CHEM global model as a function of local aerosol composition, temperature, and relative humidity. We find a much lower global mean γ_{N2O5} (0.02) than commonly assumed in models (0.1). Relative to a model simulation assuming a uniform $\gamma_{N2O5} = 0.1$, we find increases in mass-averaged tropospheric NO_x, O_3, and OH concentrations of 7%, 4%, and 8% respectively. The increases in NO_x and O_3 concentrations bring the GEOS-CHEM simulation in better agreement with climatological observations. **Citation:** Evans, M. J., and D. J. Jacob (2005), Impact of new laboratory studies of N_2O_5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, *Geophys. Res. Lett.*, *32*, L09813, doi:10.1029/2005GL022469.

1. Introduction

[2] Reactive oxides of nitrogen ($NO_x \equiv NO + NO_2$) play a defining role in the chemistry of the troposphere. They react catalytically to produce ozone (O_3) and OH, the main tropospheric oxidants. The dominant global source of NO_x is the burning of fossil fuel (20–33 Tg N yr^{-1}) with minor contributions from biomass and biofuel burning (collectively 3–13 Tg N yr^{-1}), soils (4–7 Tg N yr^{-1}), and lightning (3–13 Tg N yr^{-1}) [*Intergovernmental Panel on Climate Change* (*IPCC*), 2001]. NO_x is permanently removed from the atmosphere by conversion to nitric acid followed by deposition. During the day, this conversion occurs through the reaction of NO_2 with OH, and during the night by hydrolysis of N_2O_5 in aerosols. These mechanisms are globally comparable as sinks of NO_x [*Dentener and Crutzen*, 1993]. Previous evaluations of the literature based upon work undertaken for stratospheric conditions [*Jacob*, 2000] gave a best estimate of 0.1 for the reaction probability of N_2O_5 (γ_{N2O5}), i.e. the probability that a N_2O_5 molecule impacting an aerosol surface undergoes reaction. This value has been the standard used in many tropospheric chemistry models [*Dentener and Crutzen*, 1993; *Wang et al.*, 1998; *Bey et al.*, 2001; *Tie et al.*, 2001; *Stroud et al.*, 2003]. A study by *Tie et al.* [2003] found that $\gamma_{N2O5} = 0.04$ or less gave a better simulation of NO_x concentrations observed during the TOPSE aircraft campaign over the North American Arctic. Photochemical model analyses of observed NO_x/HNO_3 ratios in the upper troposphere have also suggested that γ_{N2O5} is much less than 0.1 [*McKeen et al.*, 1997; *Schultz et al.*, 2000]. Recent laboratory studies of N_2O_5 hydrolysis [*Kane et al.*, 2001; *Hallquist et al.*, 2003; *Thornton et al.*, 2003] provide sufficient information to improve the representation of γ_{N2O5} in global models as a function of local aerosol composition, relative humidity (R.H.), and temperature. We examine here the implications for model simulations of the global tropospheric budgets of NO_x, O_3, and OH.

2. Model Calculation of N_2O_5 Reaction Probability

[3] Our analysis uses the GEOS-CHEM chemical transport model (CTM) which has been used previously for a number of studies focused on tropospheric O_3-OH-NO_x budgets [e.g., *Bey et al.*, 2001; *Martin et al.*, 2003a; *Hudman et al.*, 2004]. We use GEOS-CHEM version 5-07-08 (http://www-as.harvard.edu/chemistry/trop/geos). This version of the model considers five different aerosol components: dust, sulfate, organic carbon, black carbon, and sea salt. The sulfate aerosol mass concentration is calculated within the model [*Park et al.*, 2004] and the mass concentration of the other components are specified as 3-D monthly mean values from the GOCART model [*Chin et al.*, 2000a, 2000b; *Ginoux et al.*, 2001; *Martin et al.*, 2003b]. Size distributions for all aerosol components are specified as described by [*Martin et al.*, 2003b].

[4] Past applications of GEOS-CHEM have assumed $\gamma_{N2O5} = 0.1$ for all aerosol types and conditions. In the present study we specify γ_{N2O5} for different aerosol components and conditions on the basis of recent laboratory studies [*Kane et al.*, 2001; *Hallquist et al.*, 2003; *Thornton et al.*, 2003]. *Kane et al.* [2001] investigated the effect of R.H. over the range 8–92% on γ_{N2O5} for ammonium sulfate, ammonium bisulfate, and sulfuric acid aerosols. We assume here that atmospheric sulfate aerosol is mainly present as ammonium sulfate, a reasonable assumption at least over continental regions [*Martin et al.*, 2004] where N_2O_5 hydrolysis is globally most important. *Kane et al.* [2001] found that γ_{N2O5} increases smoothly from 9.4×10^{-4} at 8% R.H. to 0.042 at 92%. *Hallquist et al.* [2003] investigated the effect of temperature and found that γ_{N2O5} for ammonium sulfate had a roughly constant value of 0.03 up to 280 K with a rapid decrease to 0.003 at 308 K. For our study we have adopted the R.H. parameterization of *Kane et al.* [2001] and the temperature dependence of *Hallquist et al.* [2003]. *Thornton et al.* [2003] investigated N_2O_5 uptake by organic aerosols using malonic acid particles. They found γ_{N2O5} on solid aerosol (R.H. between 0 and 50%) to be 0.001. For aqueous aerosols, γ_{N2O5} increased from

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Table 1. GEOS-CHEM Representation of the Reaction Probability γ_{N2O5} for N_2O_5 Hydrolysis on Aerosol Surfaces

Aerosol Type	Reaction Probability[a]	Reference
Sulfate[b]	$\gamma = \alpha \times 10^{\beta}$	*Kane et al.* [2001]
	$\alpha = 2.79 \times 10^{-4} + 1.3 \times 10^{-4} \times RH - 3.43 \times 10^{-6} \times RH^2 + 7.52 \times 10^{-8} \times RH^3$	
	$\beta = 4 \times 10^{-2} \times (T-294)$ $(T \geq 282K)$	*Hallquist et al.* [2003][c]
	$\beta = -0.48$ $(T < 282K)$	
Organic carbon	$\gamma = RH \times 5.2 \times 10^{-4}$ $(RH < 57\%)$	*Thornton et al.* [2003][d]
	$\gamma = 0.03$ $(RH \geq 57\%)$	
Black carbon	$\gamma = 0.005$	*Sander et al.* [2003]
Sea salt	$\gamma = 0.005$ $(RH < 62\%)$	*Sander et al.* [2003][e]
	$\gamma = 0.03$ $(RH \geq 62\%)$	
Dust	$\gamma = 0.01$	*Bauer et al.* [2004][f]

[a]T is temperature (K), RH is relative humidity (%).

[b]We assume a separable relationship between R.H. and temperature effects on γ_{N2O5}, using the work by *Kane et al.* [2001] for the R.H. effect and *Hallquist et al.* [2003] for the temperature effect.

[c]Logarithmic fit of data presented in Figure 11 of *Hallquist et al.* [2003].

[d]Linear fit of data presented in Figure 6 of *Thornton et al.* [2003].

[e]We use the work of *Sander et al.* [2003] for the reaction probability on dry and aqueous sea-salt aerosol, and assume that the aerosol is dry for RH < 62%, corresponding to the midpoint between deliquescence and efflorescence R.H. [*Martin*, 2000].

[f]No value available from published literature. *Bauer et al.* [2004] quote a range from 0.003 to 0.02 from unpublished measurements by J. Crowley as part of the MINATROC EU Commission project EVK2-CT-1999-00003.

0.01 to 0.03 as R.H. increased from 20 to 50%, (between 20 and 50% R.H. a metastable state exists) with values remaining constant at around 0.03 for R.H. above this. It appears that for much of the atmosphere organic aerosols are aqueous [*Bradan and Abbatt*, 2004; *Marcolli et al.*, 2004] so we assume here the aqueous range of values.

[5] Table 1 describes the updated parameterization of γ_{N2O5} in GEOS-CHEM based on these and other data. We present here results from two one-year GEOS-CHEM simulations for 2001. The first simulation uses a uniform $\gamma_{N2O5} = 0.1$ and the second uses the parameterization described in Table 1. Both simulations were initialized with a 12-month spin-up. The horizontal resolution used is 4° × 5° and there are 30 vertical layers from the surface to 50 hPa. Further details of the tropospheric chemistry simulations in GEOS-CHEM are presented, for example, by *Bey et al.* [2001] and *Martin et al.* [2003a].

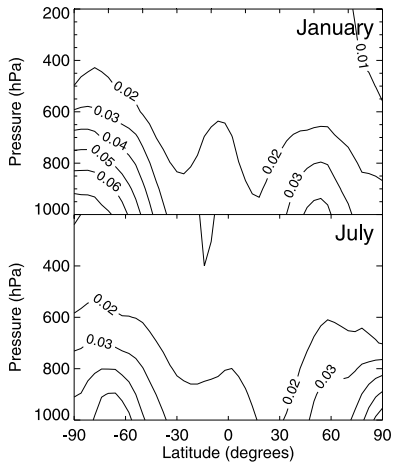

Figure 1. Zonal mean N_2O_5 reaction probabilities (γ_{N2O5}) for January and July 2001, calculated in the GEOS-CHEM global model using the expressions of Table 1.

[6] Figure 1 shows the zonal mean γ_{N2O5} values for January and July as computed in GEOS-CHEM from the data in Table 1. γ_{N2O5} for each grid-box is calculated as the mean γ_{N2O5} over all aerosol components weighted by the relative contribution of each component to the total aerosol surface area of that grid-box. Much of the spatial and seasonal variability in Figure 1 reflects the temperature and R.H. dependences of γ_{N2O5} on sulfate aerosol. Values are highest in surface air at the summertime poles and at northern mid-latitudes in winter because of cold temperatures, high R.H., and a large contribution of sulfate to the total aerosol surface area. The general decrease of γ_{N2O5} with altitude is due to the decrease in R.H., leading to minima in the very low R.H. downward branches of the Hadley circulation. The global mean γ_{N2O5} is 0.02. During the spring months in the Arctic, γ_{N2O5} ranges from 0.01 to 0.04 which is within the range found by *Tie et al.* [2003] to match the TOPSE NO_x observations. The low values in the upper troposphere (~0.01) are consistent with HNO_3/NO_x concentration ratios measured from aircraft [*McKeen et al.*, 1997; *Schultz et al.*, 2000].

3. Impact on Global Model Budgets

[7] Figure 2 shows the calculated zonal mean fractional change in the concentrations of NO_x, O_3 and OH for Dec–Feb and Jun–Aug with the new parameterization for γ_{N2O5},

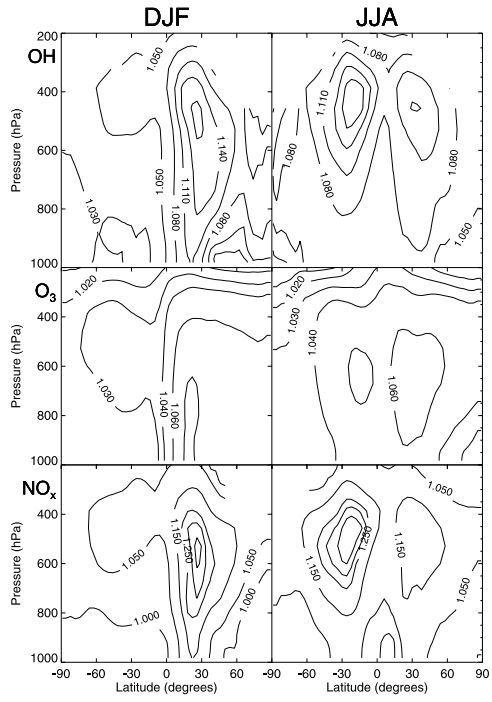

Figure 2. Calculated zonal mean concentration ratios of OH, ozone, and NO_x for GEOS-CHEM model simulations with γ_{N2O5} values calculated from Table 1 versus a uniform value of 0.1. Results are seasonal averages for winter (DJF) and summer (JJA). Values greater than 1 indicate higher concentrations with the γ_{N2O5} values calculated from Table 1 than with a uniform γ_{N2O5} of 0.1.

as compared to the simulation with $\gamma_{N2O5} = 0.1$. The tropospheric NO_x burden increases from 9.6 Gg N to 10.2 Gg N (7%). The largest increases (~50%) are found in winter in the downward branch of the Hadley circulation, consistent with the reduction in γ_{N2O5} associated with these dry warm conditions (Figure 1). On a global mass-weighted basis, N_2O_5 concentrations are 250% higher and NO_3 concentrations are 30% higher. Comparison of model results with a compilation of aircraft observations of NO_x concentrations mapped onto a monthly $4° \times 5°$ grid [*Emmons et al.*, 2000] shows a reduction in the mass-weighted model bias from −14.0 pptv to −7.9 pptv with the new γ_{N2O5} parameterization. The mean ratio of simulated to observed NO_x concentrations for that compilation increases from 0.77 to 0.86. The largest change is in the middle troposphere (3–10km) where the mean ratio increases from 0.79 to 0.91.

[8] Simulated O_3 concentrations increase with the new N_2O_5 hydrolysis parameterization, responding to the increased NO_x concentrations. The total burden of tropospheric O_3 increases by 4% from 249 Gg to 260 Gg. Comparison with the climatological compilation of tropospheric ozonesonde data by [*Logan*, 1999] shows a reduction in the mass-weighted model bias from −2.9 ppbv to −1.4 ppbv. The mass-weighted model to measured concentration ratio improves from 0.94 to 0.99. The global O_x (odd oxygen) chemical production increases within the troposphere by 7% from 3900 Tg O_3 yr^{-1} to 4180 Tg O_3 yr^{-1}. An intercomparison between 10 global tropospheric chemistry models [*IPCC*, 2001] found a global mean O_x production rate of 3365 ± 745 Tg O_3 yr^{-1} across all the models. GEOS-CHEM is at the high end of this range, but we have argued that this could reflect biases in other models [*Bey et al.*, 2001].

[9] The combined effect of increasing the NO_x and O_3 concentrations is an increase in the concentration of OH. The mass-weighted, global annual mean tropospheric OH concentration increases from 0.99×10^6 cm^{-3} to 1.08×10^6 cm^{-3} (an 8% increase). Both values are consistent with the current constraints on global mean OH concentrations based on methyl-chloroform observations: $1.07\ (^{+0.09}_{-0.17}) \times 10^6$ cm^{-3} [*Krol et al.*, 1998], $1.16 \pm 0.17 \times 10^6$ cm^{-3} [*Spivakovsky et al.*, 2000], and $0.94 \pm 0.13 \times 10^6$ cm^{-3} [*Prinn et al.*, 2001].

[10] The new parameterization for γ_{N2O5} described in Table 1 thus has significant impact on simulations of tropospheric composition and points to the need for further work to characterize N_2O_5 uptake by aerosols. There are to our knowledge no laboratory data for γ_{N2O5} on dust aerosols, which make a large contribution to total aerosol surface area. Uncertainties in organic aerosol phase, and in the mixing states between different aerosol types, are also major issues.

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